



# Synthesis and Characterization of Cobalt-Containing Nanoparticles on Alumina: A Potential Catalyst for Gas-to-Liquid Fuels Production

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## **Abstract**

Fisher-Tröpsch synthesis (FTS) is a century-old gas-to-liquid (GTL) technology that commonly employs cobalt (Co, on an oxide support) or iron (supported or not) species catalysts. It has been well established that the activity of the Co catalyst depends directly upon the number of surface Co atoms. The addition of promoter (mainly noble) metals has been widely utilized to increase the fraction of Co that is available for surface catalysis. Direct synthesis of Co nanoparticles is a possible alternative approach; our preliminary synthesis and characterization efforts are described. Materials were characterized by various transmission microscopies and energy dispersive spectroscopy. Tri-n-octylphosphine oxide (TOPO) and dicobalt octacarbonyl were heated under argon to a temperature of 180 °C with constant stirring for 1 hr. Quenching the reaction in toluene produced Co-containing nanoparticles with a diameter of 5 to 10 nm. Alternatively, an alumina support (SBA-200 Al<sub>2</sub>O<sub>3</sub>) was added; the reaction was further stirred and the temperature was decreased to 140 °C to reduce the rate of further growth/ripening of the nucleated Co nanoparticles. A typical size of Co-containing NPs was also found to be in the range of 5 to 10 nm. This can be contrasted with a range of 50 to 200 nm for conventionally-produced Co-Al<sub>2</sub>O<sub>3</sub> Fischer-Tröpsch catalysts. This method shows great potential for production of highly dispersed catalysts that are either supported or unsupported.

## Introduction

Fisher-Tröpsch synthesis (FTS) is a century-old gas-to-liquid (GTL) technology that commonly employs Co (on an oxide support) or Fe (supported or not) species catalysts. The raw material is a gaseous mixture of CO and H<sub>2</sub> (synthesis gas or syngas) typically produced by the slightly exothermic partial oxidation of methane (1). Through FTS, a syngas feedstock is converted into various liquid hydrocarbons (2) (Ref. 1).



It has been well established that the catalytic activity of the cobalt catalyst depends directly upon the number of surface cobalt (Co) atoms as determined by hydrogen chemisorption. The turnover number (TON) remains constant as the cobalt dispersion increases up to about 12 percent (Ref. 2). Since the TON is constant with Co dispersion, approaches to increase catalyst productivity include increasing dispersion and/or increasing the fraction of cobalt that is reduced to the metal. The addition of promoter (mainly noble) metals has been widely utilized to increase the fraction of cobalt that is available for surface catalysis (Ref. 3). Direct synthesis of Co nanoparticles is a possible alternative approach; our preliminary synthesis and characterization efforts are described.

## Experimental Details and Results

All chemicals were used as received. Tri-n-octylphosphine oxide (TOPO, Alfa Aesar) (73.46 g, 0.19 moles) was added to a three neck (24/40) 300 mL round-bottom flask (RBF) containing 150 mL of toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, Sigma-Aldrich) and heated under argon to a temperature of 180 °C with constant stirring for 1 hr. Separately, 6.5 g (1.9×10<sup>-3</sup> moles) of dicobalt octacarbonyl (Co<sub>2</sub>(CO)<sub>8</sub>, Strem Chemicals) was added to a 50 mL RBF in an inert atmosphere glovebox (Vacuum Atmospheres). Moderate application of a heating gun was employed to aid dissolution of Co<sub>2</sub>(CO)<sub>8</sub> in 30 mL of toluene.

An addition funnel was added to the 300 mL RBF and heated prior to adding Co<sub>2</sub>(CO)<sub>8</sub> solution to ensure the compound did not precipitate out upon loading via the addition funnel. The Co<sub>2</sub>(CO)<sub>8</sub> solution was then added to the TOPO solution under constant stirring and constant temperature of 180 °C at rate of approximately 2 drops/sec. *Note: vent the reaction vessel at this step due to the immediate out-gassing of CO, this is especially critical if the Co<sub>2</sub>(CO)<sub>8</sub> solution is added rapidly.* Upon completion of the addition of the Co solution, the reaction was stirred for 1 hr; a 2 mL aliquot was then withdrawn and quenched in 10 mL of toluene for TEM analysis. A schematic diagram and photograph of CO nanoparticle samples is shown in Figure 1(a) and (b), respectively. Transmission electron micrographs (Phillips CM-20) are shown in Figure 2.

Immediately after the removal of the aliquot, 7.72 g of SBA-200 alumina (Al<sub>2</sub>O<sub>3</sub>, Sasol) was added with the aid of a paper funnel. The reaction was further stirred and the temperature was decreased to 140 °C to reduce the rate of further growth/ripening of the nucleated Co nanoparticles. The solution was held at 140 °C for 3 hr with continuous stirring. The temperature was lowered to 100 °C and the stirring ended.

After 1 hr sitting at 100 °C without stirring, the contents were transferred to an alumina boat and placed inside a tube furnace under a constant flow of argon (1.5 slpm). The furnace was heated to 230 °C (the controller was actually set to 255 °C because the thermocouples were placed inside the furnace heating elements, but outside the inner calcination tube) and held at this temperature for 2 hr. This processing step is added to decompose the organic constituents and facilitate binding of Co-NPs to the substrate. Figure 3 compares a standard FT catalyst (Ref. 3) with a typical Co-containing NP-loaded alumina substrate.

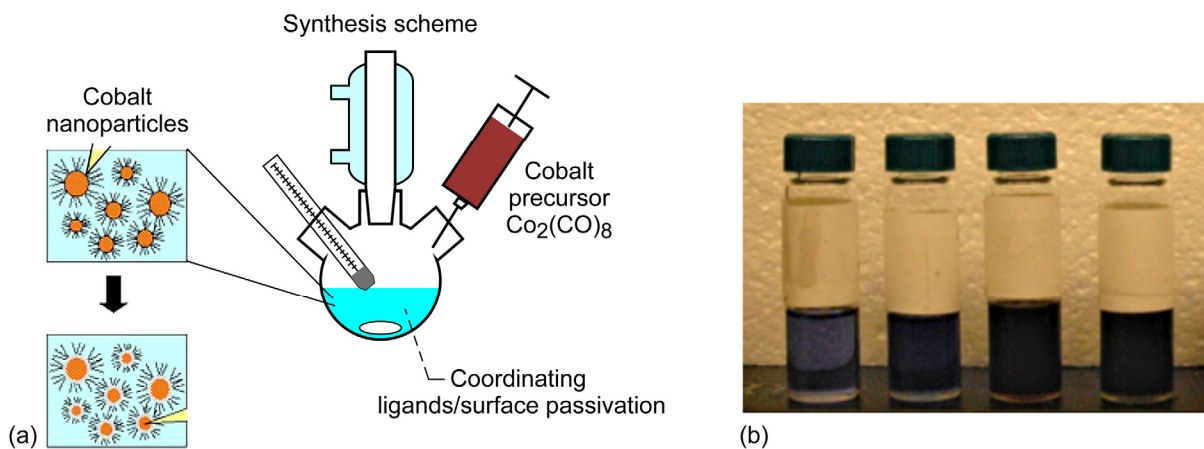


Figure 1.—(a) Diagram of typical synthesis of Co nanoparticles; (b) Aliquots from reaction quenched in toluene.

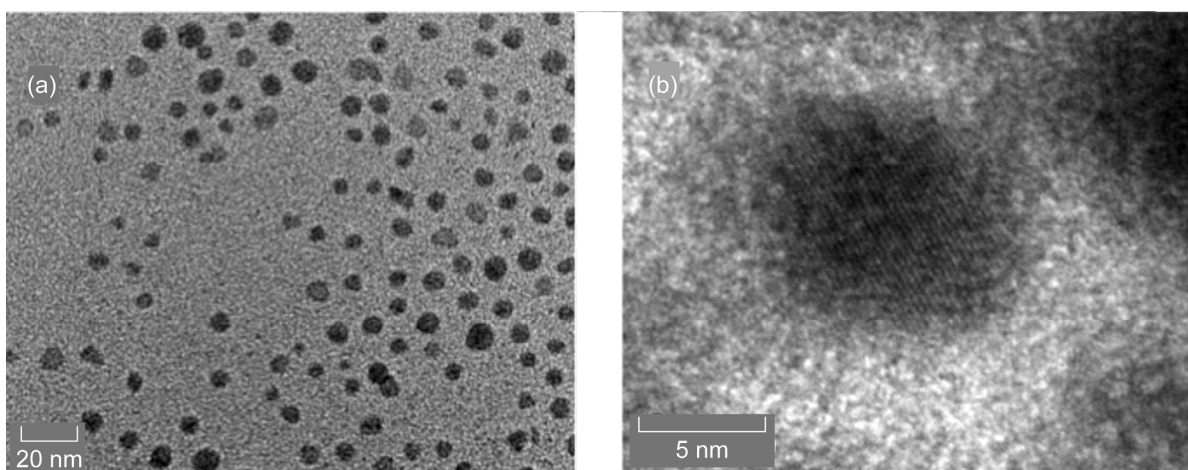


Figure 2.—(a) Bright field (left) and (b) high-resolution transmission electron micrographs (right) of typical Co nanoparticles.

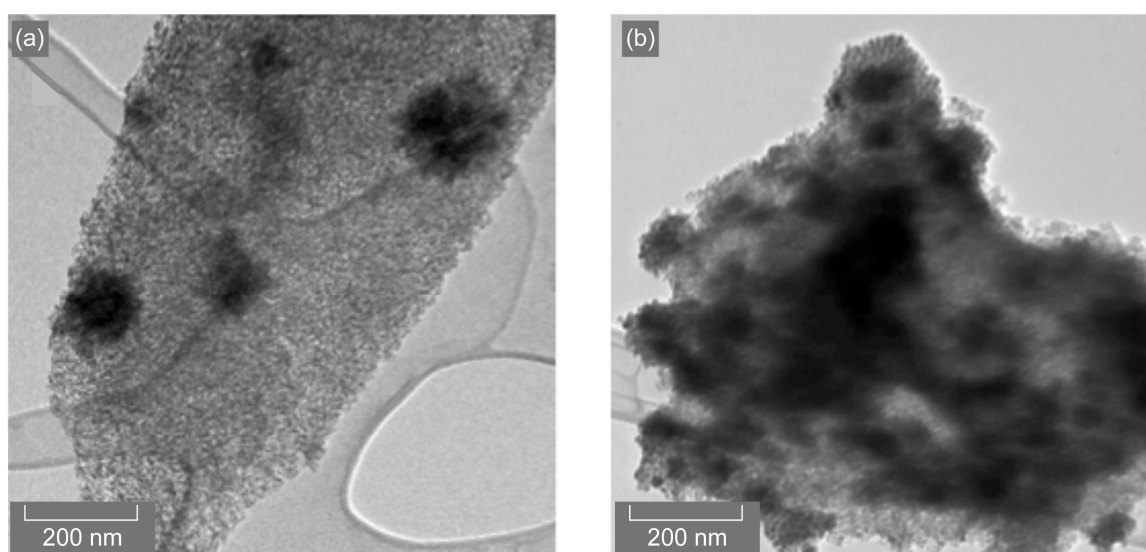


Figure 3.—Bright field TEM images comparing (a) typical standard  $\text{Co}/\text{Al}_2\text{O}_3$  FT catalyst (left) with (b) Co NP/ $\text{Al}_2\text{O}_3$  samples (right).



A HR-TEM bright field image (Fig. 4) yields a typical crystallite size of 5 to 10 nm for Co-containing nanoparticles. These are similar in size to the toluene-quenched Co-containing nanoparticles shown above (Fig. 2), and quite a bit smaller than the conventionally-processed Co-Al<sub>2</sub>O<sub>3</sub> catalyst above (Fig. 3). While we did not analyze the oxidation state of the Co-containing nanoparticles, these are most likely CoO (Refs. 1 to 3).

Confirmation of the identity of the nanoparticles and substrate materials was made by scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDS) (Fig. 5). Note that the darker features are predominantly Co-containing while lighter-shaded areas contain both Al and Co.

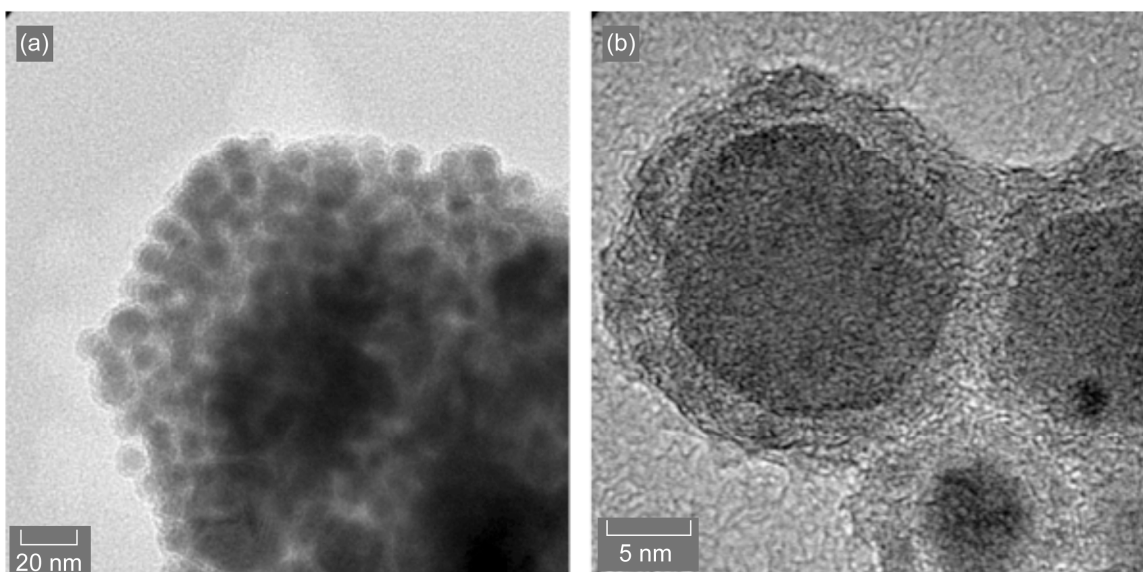


Figure 4.—(a) Bright field TEM images of Co-containing NP/Al<sub>2</sub>O<sub>3</sub> sample shown in Figure 3(b) on left and (b) at higher magnifications on right.

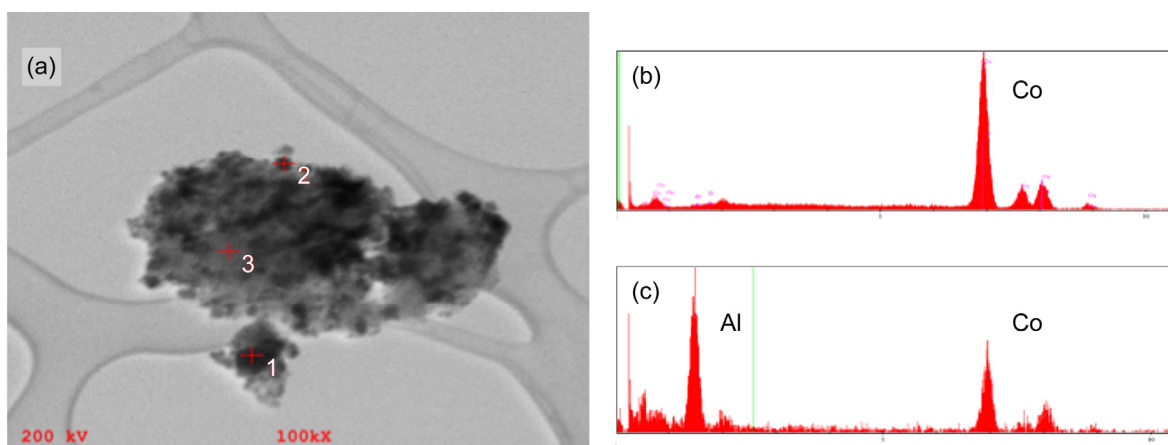


Figure 5.—(a) Scanning transmission electron microscopy (STEM) image (left) and on right, corresponding energy dispersive spectra (EDS) of (b) regions 1 (top) and (c) 3 (bottom).



## Discussion

Earlier use of TOPO and related compounds was reported for industrial extractions (Ref. 4) such as reprocessing of nuclear fuels (Ref. 5); early reports for producing quantum dots or semiconductor nanoparticles of III-V compounds are found in 1996 (Ref. 6). Our work indicates that TOPO not only plays an important role (well known in field of colloidal chemistry) in synthesizing Co nanoparticles uniform in size and morphology, but also could potentially play a vital role for the fabrication of highly disperse Co NP/alumina-catalyst structures.

One of the current problems when preparing catalysts by conventional methods previously described occurs as the Co agglomerates or ripens during calcination resulting in catalysts with poor dispersion (Refs. 1 to 3). The use of TOPO as a capping group for the synthesis of Co nanoparticles dispersed onto alumina circumvents these issues as its extremely low-volatility (Refs. 4 to 6) allows sufficient time for the metallic Co to bind to the alumina support before the TOPO is released in the calcination process. The low volatility of TOPO dictates that the calcination temperature has to be a minimum of 230 °C for its effective removal.

## Conclusions

Co-containing NPs have been synthesized in the presence of the highly coordinating ligand TOPO. Nanoparticle formation can be quenched in toluene. Alumina substrates can also support these Co-containing nanoparticles. Typical crystallite sizes for both supported and unsupported Co-containing NPs are below 10 nm as compared to 50 to 200 nm for conventionally-processed FT catalysts. This method shows great potential for production of highly dispersed catalysts that are either supported or unsupported. Further process improvement(s) should enable finer control of size and distribution.

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